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XIV.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON CERTAIN DERIVATIVES OF PYROMUCAMIDE.

By Charles E. Saunders.

Presented by Henry B. Hill, November 9, 1892.

This investigation was undertaken at the suggestion of Professor H. B. Hill, in the hope of obtaining from pyromucamide or its derivatives, through Hofmann's * reaction, an amine having the nitrogen atom directly united to a carbon atom of the furfuran ring, no such amine being at present known. Since preliminary experiments with pyromucamide had shown that the reaction was complicated by products formed through the action of the bromine upon the furfuran group, βδ-dibrompyromucamide was chosen as better adapted to the purpose, since the corresponding acid is unaffected by bromine. In this case, however, the product proved to be the nitrile of the acid, instead of the amine, with one less carbon atom. The behavior of pyromucamide with dry bromine was next studied, and a stable tetrabromide isolated, and at the same time the action of bromine in aqueous solution upon pyromucamide was examined in order to find an explanation of certain striking color reactions which had previously been observed in this Laboratory.

The Action of Bromine and Potassium Hydroxide on βδ-Dibrompyromucamide.

Bromine alone has no marked action on βδ-dibrompyromucamide, the amide dissolving quietly in the bromine. On evaporating, the amide can be recovered unchanged, though the removal of the last portions of bromine at ordinary temperatures occupies considerable time, indicating perhaps the production of an unstable tetrabromide. Nevertheless, all attempts to prove more definitely the formation of such a product failed. When the amide was dissolved in bromine and the solution treated with aqueous potassium hydroxide, a small yield of a substance insoluble in water was obtained. This was filtered off, washed with water, and distilled with steam. The best yield was obtained as follows. One part of the amide was dissolved in 1.8 parts of bromine (about six atoms of bromine to one molecule of amide) in a large beaker. Over this solution was poured a considerable quantity of a cold five per cent solution of sodium or potassium hydroxide. The contents of the beaker were kept cold, and allowed to stand, the alkaline reaction being maintained by the occasional addition of a small portion of 20 per cent sodium hydroxide solution. The insoluble product gradually rose to the surface, as the bromine disappeared, and was skimmed off. It was washed with dilute acid, and then distilled with steam. The yield was nearly 13 per cent of the weight of amide taken. For further purification the substance was crystallized from a very small quantity of alcohol, solution being brought about at 90° to 100° under pressure.

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* Berichte der deutsch. chem. Gesellsch., XIV. 2725; XV. 407, 752, 762; XVII. 1406, 1923; XVIII. 2734.

The substance gave the following results on analysis: —

I. 0.4259 grm. substance gave 0.3745 grm. CO_2 and 0.0160 grm. H_2O.

II. 0.2044 grm. substance gave 0.3082 grm. Ag.Br.

III. 0.2056 grm. substance gave 10.3 c. c. of moist nitrogen at 15°.3 and 757.5 mm. pressure.

	Calculated for C_5HBr_2NO.	Found. I.	II.	III.
C	23.90	23.98		
H	0.40	0.42		
Br	63.75		64.17	
N	5.58			5.84

The analysis shows that the substance is not the expected amine, but is βδ-dibromfurfuronitrile. This conclusion was confirmed by the reactions of the substance, and by its preparation through the dehydration of the amide, using phosphorus pentachloride as the dehydrating agent. The amide was mixed with the calculated quantity of phosphorus pentachloride, and the mixture heated in a distilling flask to about 200°, until hydrochloric acid ceased to be given off. The contents of the flask were then distilled with steam. The yield of dibromfurfuronitrile was 56 per cent of the calculated amount. The substance as thus obtained was found to be identical in composition and physical properties with that formed by the action of bromine and dilute potassium hydroxide on the dibromamide. A combustion of this product gave the following results: —

0.4272 grm. substance gave 0.3793 grm. CO_2 and 0.0217 grm. H_2O.

	Calculated for C_5HBr_2NO.	Found.
C	23.90	24.21
H	0.40	0.56

Properties of βδ-Dibromfurfuronitrile. — It is a colorless solid, possessing a characteristic and rather pleasant odor. It is volatile with steam, scarcely at all soluble in water, readily soluble in ether and in hot alcohol (especially at 100° under pressure). Its melting point is 88° (uncor.), and its boiling point 225° (uncor.). It can be sublimed. It crystallizes from superheated alcohol in leaflets or plates. On standing for several days in a warm room with concentrated hydrochloric acid, it is converted into βδ-dibrompyromucamide. When it is heated for about an hour in a sealed tube at 100° with concentrated hydrochloric acid, a considerable amount of βδ-dibrompyromucic acid is formed. Prolonged heating causes blackening.

These two reactions were tried with the nitrile prepared in both ways. In alcoholic solution sodium amalgam formed no reduction product. The nitrile was dissolved in dilute alcohol, and treated with two per cent sodium amalgam, a current of carbon dioxide being passed through until the action was over. The distillate obtained from this was not alkaline, and gave practically no residue when acidified and evaporated. The residue in the flask gave, on evaporation, needles of βδ-dibrompyromucamide.

When the solution of dibromamide in bromine was treated with dilute cold potassium or sodium hydroxide, the only product found, beside the nitrile, was monobrommaleic acid. This was identified by its melting point and other physical properties, as well as those of its barium salt.

The dehydration of the dibromamide, — under the conditions of the experiments related, — with formation of the nitrile, is particularly interesting, because Hofmann * found that, in preparing amines from amides by the method introduced by him, nitriles were sometimes produced, chiefly when working with the amides of the higher fatty acids; but the nitriles thus formed always contained one carbon atom less than the amide with which he started, and he considers the amine to be an intermediate product in these cases. In the present instance, however, since the nitrile contains the same number of carbon atoms as the amide, this interpretation of the reaction cannot be applied. The author has no explanation to offer. It is worthy of note that the same reaction takes place, whether the alkali used is potassium, sodium, or barium hydroxide.

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* Berichte der deutsch. chem. Gesellsch., XVII. 1406, 1920.

The Action of Bromine on Pyromucamide.

The tetrabromide of pyromucamide is obtained by dropping small portions of powdered pyromucamide into bromine kept cooled below zero. One should use 3.6 parts of bromine to one part of pyromucamide; that is, about five atoms of bromine to one molecule of pyromucamide. The liquid becomes thick and should be well stirred. After the pyromucamide has all been added, the excess of bromine is allowed to evaporate, and cold alcohol poured over the well cooled residue. On standing, a pale yellow, finely divided solid is separated from the dark mass. After the latter has been completely broken up, the product is filtered off and washed with ether. The yield is between 50 and 60 per cent of the calculated amount. For further purification the substance is dissolved in ethyl acetate or acetone, and the greater part of the solvent distilled off. It is then filtered, and washed again with ether. The substance is thus obtained in minute, colorless, glistening crystals. An analysis gave the following results: —

I. 0.3417 grm. substance gave 0.1751 grm. CO_2 and 0.0410 grm. H_2O.

II. 0.1110 grm. substance gave 0.1950 grm. AgBr.

III. 0.4586 grm. substance gave 13.6 c.c. of moist nitrogen at 23°.5 and 765 mm. pressure.

	Calculated for $C_5H_5NBr_4O_2$.	Found. I.	II.	III.
C	13.92	13.98		
H	1.16	1.33		
Br	74.25		74.76	
N	.25			3.36

The substance is therefore the tetrabromide of pyromucamide.

Properties of Pyromucamide Tetrabromide. — It is a crystalline solid without color or odor. Its melting point is about 121°, as determined in the ordinary way, but it varies with the rapidity of the heating. By long heating the substance will melt, always with evident decomposition, even below 100°. It is insoluble in water, almost insoluble in ether, chloroform, glacial acetic acid, or alcohol, somewhat more readily soluble in ethyl acetate and acetone. It is decomposed by boiling with water, alcohol, or glacial acetic acid. When it was dissolved in alcohol and treated with zinc dust in the cold, the bromine was abstracted and pyromucamide formed. On boiling with water it is decomposed; hydrobromic acid is formed, but no definite organic compound could be isolated. In order to study the products formed by the action of alkalies, the tetrabromide was added gradually, in small portions, to *cold* concentrated alcoholic sodium hydroxide. After standing in the cold for about an hour, the mixture was allowed to remain for several days in a warm room, the alcohol being renewed when necessary. Ammonia was slowly evolved. The alcohol was then evaporated off, and the solid residue treated with water. Only a very small portion of insoluble matter was left. This was filtered off. On acidifying the filtrate, an acid was precipitated which was purified by converting it into the barium salt, and separating the latter by fractional crystallization into three portions. The acid was then liberated from each portion separately. It appeared to be $\beta\gamma$-dibrompyromucic acid, since each fraction melted at about 192°, the purest at 191°.5. To remove all doubt, this portion was dissolved in absolute alcohol, and converted into the ethyl ester by the action of dry hydrochloric acid. The observed melting point of the ester, 67°.5, completed the proof as to the nature of the acid, since the $\beta\gamma$-dibrompyromucic acid melts at 191–192°, and its ethyl ester at 67–68°.* $\beta\delta$-dibrompyromucic acid does not seem to be formed at all in this decomposition of pyromucamide tetrabromide. Even microscopic examination failed to prove its presence, though the crystals are quite characteristic. This is interesting in consideration of the fact observed by Hill and Sanger,* that the tetrabromide of pyromucic acid yields, under similar circumstances, a mixture of the two isomeric dibrompyromucic acids ($\beta\gamma$ and $\beta\delta$).

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* These Proceedings, XXI. 155 *et seq.*

The Action of Bromine Water on Pyromucamide.

Some remarkable color reactions observed by Professor Hill, when studying the action of bromine and potassium hydroxide on pyromucamide, led to the suggestion that interesting results might be obtained in that direction by further work. The author therefore gave a short time to the study of the nature of these color reactions, as well as those produced when bromine water is used in place of pure bromine, and when other basic substances are used in place of potassium hydroxide.

Pyromucamide treated with bromine water dissolves readily, producing a solution almost or quite colorless. This was treated in various ways in order to isolate, if possible, some definite substance from it, but amorphous dark products were always obtained. If to the fresh solution there is added almost any strongly basic inorganic substance, a dark blue (or sometimes purple) color is soon produced, the rapidity of its production depending apparently on the strength of the base. The color usually changes to purple in a short time, and afterwards undergoes other alterations, generally passing to red, and finally, if the amount of pyromucamide used is small, fading to pale yellow. When the base employed is barium hydroxide, a dark blue amorphous precipitate is produced. An investigation was made as to the quantity of bromine required to produce the maximum intensity of color from a given amount of pyromucamide. Measured quantities of dilute solutions of pyromucamide and bromine were mixed, shaken, and allowed to stand a few moments. Then an excess of sodium hydroxide was added, and the colors produced were compared. It was found that two atoms of bromine to each molecule of pyromucamide gave the deepest color on subsequent treatment with alkali. Either a deficiency or an excess of bromine is unfavorable to the color production. The dark blue compound was too unstable for isolation.

The production of this color may serve as a very delicate test for pyromucamide. When one milligram of the amide is dissolved in a drop of dilute bromine water, and the solution made alkaline, the blue (or purple) color produced is quite distinct.

Chlorine water can be used instead of bromine water, but the color was not obtained when iodine or nitric acid was employed. Substituted pyromucamides, so far as investigated, do not give the color reaction: δ-methylpyromucamide, $\beta\delta$-dibrompyromucamide, and $\beta\gamma$-dichlorpyromucamide were tried.

If, instead of sodium hydroxide, an aqueous solution of aniline is added to the solution of pyromucamide in bromine water, a *reddish precipitate* is produced. This substance is not stable. It melts at about 78°, and appears to undergo decomposition when treated with alcohol even in the cold.

By substituting a saturated aqueous solution of phenyl hydrazine for aniline, a brilliant red precipitate was obtained. The most convenient method for preparing this substance is as follows. Dissolve a weighed amount of pyromucamide in as small a quantity of water as convenient; add to this bromine, a few drops at a time, shaking the flask and keeping it cool, until for each molecule of pyromucamide two atoms of bromine have been added. The bromine will be dissolved, and the solution will be almost colorless. Filter if necessary, and add a large excess of a saturated solution of phenyl hydrazine in water. Allow the mixture to stand for some time, filter off the red precipitate formed, wash with water, then with two or three small portions of alcohol, and lastly with ether. Dry over sulphuric acid or in a steam-drying oven. The yield is about 1.6 times the weight of the amide taken. The substance as thus obtained is bright red in color. It has no definite melting point, but darkens in color between 150° and 160°. It is dissolved, and probably decomposed, by aqueous or alcoholic potassium hydroxide, with a marked increase in the intensity of the red color. It is very slightly soluble in chloroform, ether, and carbon disulphide, somewhat more readily in alcohol and acetone. Boiling with alcohol and other solvents decomposes it, but it can be obtained in small scale-like crystals by making a saturated solution at 50° in alcohol or acetone, and allowing it to cool and evaporate spontaneously. The crystals are darker in color than the amorphous material, and are quite brilliant. Qualitative tests showed the absence of bromine. Analyses of the substance, both in the crystalline and the amorphous state, were made with identical results.

The material used in analyses I. and II. was crystallized from acetone, washed with ether and dried at 100°, while in analyses III. and IV. an amorphous preparation was used which had been washed successively with water, alcohol, and ether, and dried over sulphuric acid.

I. 0.3001 grm. substance gave 0.6684 grm. CO_2 and 0.1423 grm. H_2O.

II. 0.1005 grm. substance gave 17.2 c.c. of moist nitrogen at 23°.5, and 754 mm. pressure.

III. 0.1740 grm. substance gave 0.3879 grm. CO_2 and 0.0857 grm. H_2O.

IV. 0.2196 grm. substance gave 37.9 c.c. moist nitrogen at 21°.5, and 741 mm. pressure.

	Calculated for $C_{11}H_{11}N_3O_2$.	Found.			
		Crystalline.		Amorphous.	
		I.	II.	III.	IV.
C	60.83	60.74		60.80	
H	5.07	5.27		5.47	
N	19.35		19.08		19.10

The formula of the substance $C_{11}H_{11}N_3O_2$ shows that it contains the elements of one molecule of phenyl hydrazine, and one of pyromucamide, less two atoms of hydrogen. Lack of time prevented a more extended study of this body, but the investigation will be continued at some future time in this Laboratory.